

## Realization of CuInSe<sub>2</sub>/GaAs heterojunctions for photovoltaic conversion

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**Abstract** : The *p* CuInSe<sub>2</sub>/*n* GaAs heterojunctions were prepared by vacuum evaporation of CuInSe<sub>2</sub> polycrystalline powder from a single source onto (111) B surface of monocrystal GaAs substrates. Thermal treatment ( $T = 300^\circ\text{C}$ ,  $t = 10\text{ min}$ ) of heterostructures was found to result in the essential improvement of photoelectrical parameters (from  $V_{oc} = 0.22\text{ V}$ ,  $J_{sc} = 5\text{ mA/cm}^2$  to  $V_{oc} = 0.55\text{ V}$ ,  $J_{sc} = 31\text{ mA/cm}^2$  under illumination power density,  $P = 100\text{ mW/cm}^2$ ). These structures have clearly defined diode characteristics ( $K \sim 10^5$  at  $V = 1.0\text{ V}$ ) and display light sensitivity in the region  $0.50\text{--}1.05\text{ }\mu\text{m}$ . Experimental results show that, these cells have high efficiency ( $\eta = 6.3\%$ ) and are stable.

**Keywords** : Heterojunctions, photovoltaics

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### 1. Introduction

The CuInSe<sub>2</sub>/GaAs heterostructures seem to be the most prospective heterojunctions for the creation of effective, stable and inexpensive solar cells. CuInSe<sub>2</sub> component of this heterostructure possesses an optimal gap ( $\sim 1\text{ eV}$ ) corresponding to the maximum of the solar spectrum, a direct energy gap and a high absorption coefficient ( $\alpha = 10^5\text{ cm}^{-1}$  at  $h\nu > 1\text{ eV}$ ). It is a useful material for use in solar cells, optical detectors and light emitting diodes [1–3]. For the economical reasons, CuInSe<sub>2</sub> layers can be prepared in the form of thin films with large areas.

GaAs single crystal layer which makes the second component of the heterojunction has lattice parameters very close to those of the CuInSe<sub>2</sub> layer. Difference in the lattice constants of GaAs ( $a = 5.65\text{ }\text{\AA}$ ) and CuInSe<sub>2</sub> ( $a = 5.70\text{ }\text{\AA}$ ,  $c = 11.62\text{ }\text{\AA}$ ) is about 2.3 percent.

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The present work deals with the preparation of  $\text{CuInSe}_2/\text{GaAs}$  heterojunctions and the study of their photoelectric properties.

## 2. Experimental methods

$\text{CuInSe}_2/\text{GaAs}$  heterojunctions were prepared by vacuum evaporation of  $\text{CuInSe}_2$  polycrystalline powder from a single source onto chemically cleaned GaAs substrates with a thickness of 250  $\mu\text{m}$ . Substrates used in this work were monocrystal GaAs plates of  $n$ -type conductivity with carrier concentration of  $n \cong 10^{17} \text{ cm}^{-3}$ , oriented in (111)B planes. Active areas of the samples were about 10  $\text{mm}^2$ . The  $\text{CuInSe}_2$  homogenous films of stoichiometric composition were prepared at source and substrate temperatures of  $T_{\text{ev}} \geq 1300^\circ\text{C}$  and  $T_{\text{sub}} = 500^\circ\text{C}$ , respectively. X-ray analysis shows that  $\text{CuInSe}_2$  samples prepared under these conditions, possess a single phase structure. Ohmic contacts to the  $n$  GaAs plates and  $p$   $\text{CuInSe}_2$  layers were made by thermally evaporated indium in vacuum and In-Ga eutectics, respectively. After preparation, the samples were annealed in air for 10 minutes at  $300^\circ\text{C}$  which is an experimental optimal regime for these heterostructures.

## 3. Experimental results and discussion

The experimental study of electrical properties of  $p$   $\text{CuInSe}_2/n$  GaAs heterojunctions shows that these structures have clearly defined diode characteristics ( $K \sim 10^5$  at  $V = 1 \text{ V}$ ) after annealing in air at  $300^\circ\text{C}$  for 10 min. At forward bias, the current starts to rise at about 0.74 V and in the reverse direction, current tends to saturate. The analysis of direct I-V characteristics shows that the current rises according to an exponential law similar to  $I = I_s \exp\left(\frac{qV}{\beta KT}\right)$  (where  $I_s$  is the dark saturation current and  $\beta$  is the diode factor) indicating that the current flow is due to a thermal emission mechanism with  $I_s \cong 0.1 \mu\text{A}/\text{cm}^2$  and  $\beta \cong 1.5$ . The capacitance-voltage characteristics of the heterojunctions exhibit a  $1/C^2 \sim V$  law, indicating an abrupt junction.

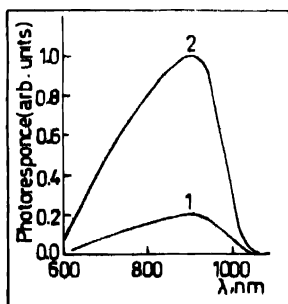


Figure 1. Optical response of a  $p$   $\text{CuInSe}_2/n$  GaAs heterojunction, before (1) and after (2) annealing in air for 10 min at  $300^\circ\text{C}$ .

In Figure 1 the spectra of the photosensitivities are given for a  $\text{CuInSe}_2/\text{GaAs}$  sample, before (curve 1) and after (curve 2) annealing. The sensitivities of the samples are in the range

0.50-1.05  $\mu\text{m}$ . For  $\lambda < 0.9 \mu\text{m}$  photosensitivity is due to the absorption in GaAs, while for  $\lambda > 0.9 \mu\text{m}$  it is due to the absorption by  $\text{CuInSe}_2$ .

The variations of current density  $J$  versus the applied voltage under illumination power density  $P = 100 \text{ mW/cm}^2$  for a  $p \text{ CuInSe}_2/n \text{ GaAs}$  heterojunction before (curve 1) and after (curve 2) annealing are given in Figure 2a. As it is seen from the figure, the thermal treatment ( $T = 300^\circ\text{C}$ ,  $t = 10 \text{ min}$ ) leads to a considerable improvement of the photoelectrical parameters of the heterojunction (from  $V_{oc} = 0.22 \text{ V}$ ,  $J_{sc} = 5 \text{ mA/cm}^2$  to  $V_{oc} = 0.55 \text{ V}$ ,  $J_{sc} = 31 \text{ mA/cm}^2$ ). Such parameters of the heterojunction give the conversion efficiency of  $\eta = 6.3\%$ . The values of efficiencies obtained for these heterostructures are rather good in comparison with the similar heterojunctions [4,5]. Investigations show that the photoelectric parameters of these heterojunctions exhibit high stability under illumination.

Essential parameters of  $p \text{ CuInSe}_2$  and  $n \text{ GaAs}$  components before and after annealing are given in Table 1.

Table 1. Essential parameters

Parameters	$n \text{ GaAs}$	$p \text{ CuInSe}_2$	
		Before annealing	After annealing
$\alpha \text{ \AA}$	5.65	5.78	5.78
$\alpha \cdot 10^6 \text{ k}^{-1}$	7.75	10.5	10.5
$E_g \text{ eV}$	1.45	1.02	1.02
$\epsilon$	13	9.3	9.3
$n \text{ p cm}^{-3}$	$10^{17}$	$10^{17}$	$10^{18}$
$\chi \text{ eV}$	4.07	4.3	4.3
$\delta \text{ eV}$	0.04	0.18	0.12
$\Phi \text{ eV}$	4.11	5.14	5.20
$V_D \text{ eV}$	0.43	0.6	0.14
	Before annealing		
	0.95		
	After annealing		

To explain the observed experimental results on the improvement of photoelectrical parameters under thermal treatment, the energy band diagram of a  $p \text{ CuInSe}_2/n \text{ GaAs}$  heterojunction has been plotted. Built on the basis of the parameters in Table 1, energy band diagram of a  $\text{CuInSe}_2/\text{GaAs}$  heterojunction before (diagram 1) and after (diagram 2) annealing are given in Figure 2b.

Thermal treatment of the samples in air, as it is seen from Table 1 leads to an increase of hole concentration in  $p \text{ CuInSe}_2$  films (from  $p \approx 10^{17} \text{ cm}^{-3}$  to  $p \approx 10^{18} \text{ cm}^{-3}$ ). This may be due to the diffusion of oxygen atoms from atmosphere, which, being a VI group element, such as selenium must exhibit acceptor property in  $\text{CuInSe}_2$  films. The energy band diagram of the heterojunction involving the hole concentration rise in  $\text{CuInSe}_2$  film is shown in

Figure 2b (diagram 2). It is seen that, in the annealed heterojunction, the greater part of the diffusion potential  $V_D(\text{CuInSe}_2)/V_D(\text{GaAs}) \cong 0.16$ , drops on GaAs. Furthermore, the hole concentration increase is followed by a decrease in the width of space-charge region in

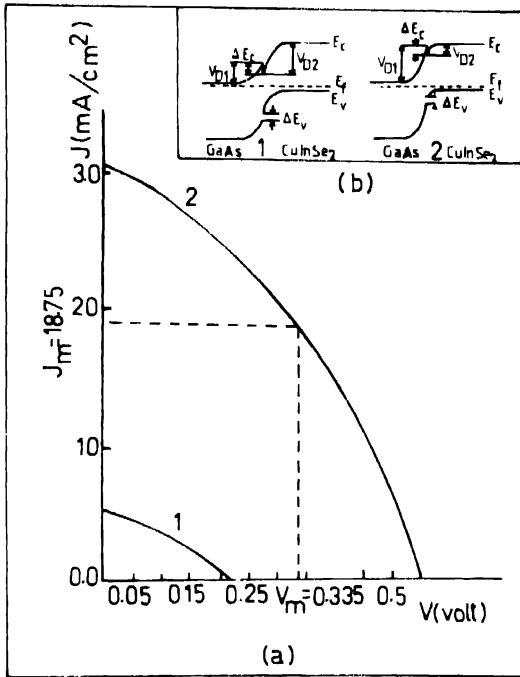


Figure 2. (a) Light  $J$ - $V$  characteristics of  $p\text{-CuInSe}_2/n\text{-GaAs}$  heterojunction before (1) and after (2) annealing in air for 10 min at 300°C. Illumination power density is  $P = 100$  mW/cm<sup>2</sup>. (b) Energy band diagrams of a  $p\text{-CuInSe}_2/n\text{-GaAs}$  heterojunction before (diagram 1) and after (diagram 2) annealing in air for 10 min at 300°C.

CuInSe<sub>2</sub> film. Therefore, the separation of photocarriers, generated in GaAs occurs very quickly, which leads to an increase of photosensitivity in the region  $\lambda < 0.9$   $\mu\text{m}$  (see Figure 1). The existence of the 'bump' in band diagram prevents the separation of photocarriers in CuInSe<sub>2</sub>, which explains the comparative low photosensitivity in the region  $\lambda > 0.9$   $\mu\text{m}$ .

#### 4. Conclusions

Investigation of the photoelectrical properties of  $p\text{-CuInSe}_2/n\text{-GaAs}$  heterojunctions prepared by vacuum deposition of CuInSe<sub>2</sub> from a single source onto GaAs substrates indicates that thermal treatment ( $T = 300^\circ\text{C}$ ,  $t = 10$  min) of these heterostructures was found to result in a considerable improvement of the photoelectrical parameters (from  $V_{oc} = 0.22$  V,  $J_{sc} = 5$  mA/cm<sup>2</sup> to  $V_{oc} = 0.55$  V,  $J_{sc} = 31$  mA/cm<sup>2</sup> under  $P = 100$  mW/cm<sup>2</sup>). Experimental results

show that, these cells have high conversion efficiency ( $\eta = 6.3\%$ ) and are stable. Energy band diagram explains the increase of conversion efficiency of the heterojunction under thermal treatment.

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